## 1, 1-Diaryl- and 1-Aryl-2-chloro-2-fluoroethylenes

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In the course of other studies in this laboratory, it became necessary to prepare some 1, 1-diaryland 1-aryl-2-chloro-2-fluoroethylenes (IV and IX). In spite of their relatively simple structure, no compounds of these types have ever been reported in the literature, except 1, 1-diphenyl- and 1, 1-bis-(p-chlorophenyl)-2-chloro-2-fluoroethylene.<sup>1</sup>) Thus, the 1, 1-diphenyl derivative has been prepared by the reaction of benzophenone with chlorofluoromethylenetriphenylphosphorane<sup>3</sup>) or by the action of chlorofluorocarbene upon diphenyldiazomethane,<sup>4)</sup> while the 1, 1-bis(*p*-chlorophenyl) derivative has been obtained from 1, 1-bis(p-chlorophenyl)-2, 2-dichloro-2-fluoroethane by dehydrochlorination.5)

This paper will describe the preparation of some

4) H. Reimlinger, Chem. Ber., 97, 339 (1964).
5) E. D. Bergmann, P. Moses, M. Neeman, S. Cohen, A. Kaluszyner and S. Reuter, J. Am. Chem. Soc., 79, 4174 (1957).

of these ethylenes via the synthetic routes shown in Fig. 1.

The starting material, methyl dichlorofluoroacetate (I), was prepared in a good yield from methyl trichloroacetate by the action of antimony trifluoride in the presence of bromine.6) It was treated with an excess of arylmagnesium bromide to give 1, 1-diaryl-2, 2-dichloro-2-fluoroethanol (II), which was then converted into the corresponding chloride III by refluxing with thionyl chloride in the presence of pyridine. The dechlorination of the product by zinc in ethanol led to one of the desired ethylenes IV.

It should be noted that the reaction of the ester I with *p*-chlorophenylmagnesium bromide resulted in a fairly good yield (58%) of the corresponding carbinol, in contrast to the observation of Bergmann et al.5) that it gave mainly 4, 4'-dichlorobiphenyl.

The hydrolysis of the ester I by sodium hydroxide gave the sodium salt of dichlorofluoroacetic acid (V), from which  $\alpha$ ,  $\alpha$ -dichloro- $\alpha$ -fluoroacetophenone derivatives (VI) were then successfully prepared by treatment with an equimolar amount

<sup>1)</sup> A number of  $\beta$ -chloro- $\beta$ -fluorostyrenes have been reported, but all of them have fluorostyrenes have been reported, but all of them have fluorine at  $\alpha$ ; see Ref. 2. 2) a) S. G. Cohen, H. T. Wolosinski and P. J. Sheuer, J. Am. Chem. Soc., **72**, 3952 (1950). b) P. Tarrant and D. A. Warner, *ibid.*, **76**, 1624 (1954). c) S. Dixon, J. Org. Chem., **21**, 400 (1956). 3) A. I. Speciale and K. W. Better, J. C.

<sup>3)</sup> A. J. Speziale and K. W. Ratts, J. Am. Chem. Soc., 84, 854 (1962).

<sup>6)</sup> E. Gryszkiewicz-Trochimowski, A. Sporzynski and J. Wnuk, Rec. trav. chim., 66, 419 (1947).



Fig. 1. Synthetic routes to gem-chlorofluoroethylenes.

TABLE 1. 1, 1-DIARYL-2-CHLORO-2-FLUOROETHYLENES AND THEIR PRECURSORS (A) 1, 1-Diaryl-2, 2-dichloro-2-fluoroethanol (II)

A _	Ýield	Вр	Mp	20-H	С,	%	Н	, %
Aryl	%	°C/mmHg	°C/mmHg °C		Calcd	Found	Calcd	Found
Phenyl <sup>5</sup>	84	150-158/5	35-36	3550	58.99	59.10	3.86	3.96
p-Tolyl	75	180-182/2	34-35	3600	61.38	61.29	4.79	4.68
p-Chlorophenyl <sup>5</sup> )	58	182 - 200/2	79-81	3560	47.51	47.65	2.54	2.67
p-Fluorophenyl	52	154-156/4	50-51	3520	52.35	52.63	2.83	2.93
p-Methoxyphenyl	59		104-105	3450	76.68	76.63	4.35	4.29

(B) 1, 1-Diaryl-1, 2, 2-trichloro-2-fluoroethane (III)

Amil	Yield	Вр	Мр	С,	%	Н,	%
Aryı	%	°C/mmHg	°Ċ	Calcd	Found	Calcd	Found
Phenyl	90	144-154/5	64-66	55.40	55.56	3.29	3.33
p-Tolyl	40		54	57.96	57.75	4.26	4.25
p-Chlorophenyl	61	200-202/3	138-140	45.15	44.98	2.15	2.21
<i>p</i> -Fluorophenyl	71	165-172/7	<10	49.50	49.23	2.38	2.58
p-Methoxyphenyl	0						

(C) 1, 1-Diaryl-2-chloro-2-fluoroethylene (IV)

Amil	Yield	Вр	Mp	$\nu_{\rm C} = c$	С,	%	Н	, %
Alyi	%	°C/mmHg	Hg °C cm <sup>-1</sup>		Calcd	Found	Calcd	Found
Phenyl <sup>3,4</sup>	78	120-124/5	36-36.5	1640	72.29	72.44	4.30	4.48
<i>p</i> -Tolyl	55		56 - 56.5	1630	73.73	73.47	5.38	5.54
p-Chlorophenyl <sup>5</sup> )	56		50-51.5	1630	55.77	55.82	2.66	2.88
<i>p</i> -Fluorophenyl	47	138—144/11	25-26	1635	62.60	62.63	2.98	2.94

of arylmagnesium bromide. Only a small amount of the corresponding carbinol was formed under the reaction conditions.7)

The Friedel-Crafts acylation with dichlorofluoro-

acetyl chloride was also attempted in preparing the ketones, but it resulted in low yields (less than 10%) of the desired products, probably due to the fluorine-chlorine exchange, as has been suggested by Bergmann et al.9)

The ketone VI was easily reduced to the corresponding carbinol VII by lithium aluminum hydride. The conversion of the resulting carbinol to the corresponding chloride VIII, followed by

<sup>7)</sup> It is well known that  $\alpha$ -fluorinated carboxylic acids or their salts give the corresponding ketones upon

<sup>actions of their saits give the corresponding kerones upon reaction with Grignard reagents; see Ref. 8.
a) K. T. Dishart and R. Levine, J. Am. Chem. Soc., 78, 2268 (1956). b) A. Sykes, J. C. Tatlow and C. K. Thomas, J. Chem. Soc., 1956, 835. c) W. Funasaka, T. Ando, T. Murase and H. Koike, Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.), 65, 1195 (1965)</sup> (1962).

<sup>9)</sup> F. Bergmann and A. Kalmus, J. Am. Chem. Soc., 76, 4137 (1954).

## TABLE 2. 1-ARYL-2-CHLORO-2-FLUOROETHYLENES AND THEIR PRECURSORS

Arvl	Yield	Вр	n <sup>t</sup> /t °C	$\nu_{\rm C} = 0$	С,	%	Н	[, %
111 91	%	°C/mmHg	$n_{\mathbf{D}}/n, \mathbf{C}$	cm <sup>-1</sup>	Calcd	Found	Calcd	Calcd Found
Phenyl <sup>2a</sup> )	50	9098/6	1.5367/21	1712	46.41	46.25	2.43	2.65
<i>p</i> -Tolyl	53	90-93/3	1.5384/21	1705	48.90	49.04	3.19	3.38
p-Chlorophenyl <sup>5</sup> )	42	97-103/5	1.5548/21	1717	39.79	39.83	1.67	1.78
<i>p</i> -Fluorophenyl	42	84-86/10	1.5129/23	1702	42.70	42.42	1.79	1.92
<i>p</i> -Methoxyphenyl	63	110-112/2	1.5615/18	1699	45.60	45.70	2.98	3.05

(A) Aryl dichlorofluoromethyl ketone (VI)

(B) 1-Aryl-2, 2-dichloro-2-fluoroethanol (VII)

	Yield	Вр	t is an	¥0-4	С, %		H, % nd Calcd Found 13 3.38 3.45 29 4.07 3.92	
Aryl	%	$%$ °C/mmHg $n_{\rm b}/t$ , °C cm <sup>-1</sup> Calcd Fo	Found	Calcd	Found			
Phenyl	85	85-95/4	1.5389/13	3360	45.96	46.03	3.38	3.45
<i>p</i> -Tolyl	72	117—118/5	1.5276/26	3400	48.47	48.29	4.07	3.92
p-Chlorophenyl <sup>5</sup> )	79	110-126/4	1.5468/21	3440	39.46	39.72	2.48	2.53
p-Fluorophenyl	65	108-110/8	1.5120/18	3380	42.32	42.09	2.66	2.68
<i>p</i> -Methoxyphenyl	62	127-128/2	1.5615/18	3350	45.21	45.08	3.79	3.91

(C) 1-Aryl-1, 2, 2-trichloro-2-fluoroethane (VIII)

A	Yield	Вр	nt it or	С,	%	Н	, %
Alyi	%	°C/mmHg	$n_{\mathbf{D}}/l, \mathbf{C}$	Calcd	Found	Calcd	Found
Phenyl	70	100-120/18	1.5349/21	42.24	42.29	2.66	2.75
<i>p</i> -Tolyl	60	97—104/4	1.5302/20	44.76	44.87	3.34	3.25
<i>p</i> -Chlorophenyl	55	107-109/4	1.5552/18	36.68	36.57	1.92	1.88
p-Fluorophenyl	69	8895/10	1.5135/20	39.14	39.22	2.06	2.22
<i>p</i> -Methoxyphenyl	56	107—111/2	1.5410/23	41.97	42.15	3.13	2.99

(D) 1-Arlyl-2-chloro-2-fluoroethylene (IX)

Arvl	Yield	Bp	$n_{\rm D}^t/t$ , °C	°C IXb/IXa $\frac{\nu_{C=C}}{cm^{-1}}$	С,	%	I	H, %	
	%	°C/mmHg	Dity -		cm <sup>-1</sup>	Calcd	Found	Calcd	Found
Phenyl	68	62-72/14	1.5320/20	1.65	1667	61.36	61.29	3.86	4.00
<i>p</i> -Tolyl	66	87-88/13	1.5404/18	1.50	1663	63.36	63.44	4.73	4.84
<i>p</i> -Chlorophenyl	62	74-84/3	1.5605/18	1.46	1661	50.30	50.49	2.64	2.65
<b>p-Fluorop</b> henyl	76	60-64/12	1.5213/20	1.60	1665	55.04	54.95	2.89	3.01
<i>p</i> -Methoxyphenyl	57	87—97/3	1.5532/23	1.46	1663	57.92	58.01	4.32	4.20

TABLE 3.	PARAMETERS	OF	ιH	NMR	SPECTRA	OF	THE	ETHYLENIC	HYDROGENS	OF	IXa	AND	IXb
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A1	IX	a	IXb			
Aryı	$\delta$ , ppm**	$J_{ m HF}^{cis}$ , cps	δ, ppm**	$J_{\rm HF}^{trans}$ , cps		
Phenyl	6.37	13.0	5.80	30.5		
p-Tolyl	6.35	13.0	5.78	31.0		
p-Chlorophenyl	6.34	12.3	5.78	30.0		
p-Fluorophenyl	6.35	13.0	5.78	30.5		
<i>p</i> -Methoxyphenyl	6.34	13.0	5.75	31.0		

\* Measured in CDCl<sub>3</sub> on a Varian A 60 spectrometer at 60 Mc.

\*\* Downfield from TMS as internal reference.

the dechlorination of the product, afforded another type of ethylene IX. As expected, the product was a mixture of two geometrical isomers, IXa and IXb; analysis by v. p. c. showed the IXb/ IXa ratio to be in the range of 1.46-1.65.

The physical properties of the ethylenes and their precursors are summarized in Tables 1 and 2, together with the yields obtained in their preparation.

The structures of IXa and IXb were determined by means of their <sup>1</sup>H NMR spectra, based on the well-established fact that the coupling constant between H and F in the -CH=CF- system is larger when they are trans than when they are  $cis.^{10}$  The coupling constants are listed in Table 3, together with the chemical shift of the ethylenic hydrogen.

Attempts were made to prepare each of the two geometrical isomers of 1-chloro-1-fluoro-2-phenylcyclopropane from IXa and IXb stereospecifically by the application of a modification of the procedure<sup>11</sup>) of the Simmons-Smith reaction, but they resulted in failure. In view of the electrophilic nature of the reaction<sup>12</sup>) and the electron-withdrawing effect of the two halogen atoms in the olefin molecule, this result does not seem surprising.

## Experimental

Methyl Dichlorofluoroacetate (I). A mixture of 305 g (1.70 mol) of methyl trichloroacetate, 202 g (1.13 mol) of antimony trifluoride, and 30 g of bromine was placed in a three-necked flask equipped with a distillation apparatus; the contents were then distilled with vigorous stirring at such a rate that the boiling point of the distillate did not exceed 120°C. After the distillate had been washed with aqueous sodium bicarbonate and with water, it was fractionally distilled to give 160 g (60%) of I (bp 117-118.5°C), together with 36 g (15%) of methyl chlorodifluoroacetate.

1, 1-Diaryl-2, 2-dichloro-2-fluoroethanol (II). To a Grignard solution prepared from 0.25 mol of an aryl bromide, 6.1 g (0.25 g-atom) of magnesium, and 250 ml of ether, a solution of 0.1 mol of I in 50 ml of ether was added gradually with stirring at -5 to 0°C. After the hydrolysis of the reaction mixture, the ether

10) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemis-try," Pergamon Press, New York (1959), p. 86. 11) E. LeCoff, J. Org. Chem., 29, 2048 (1964).

12) E. P. Blanchard and H. E. Simmons, J. Am. Chem. Soc., 86, 1337 (1964).

was distilled off from the organic layer. The residue was purified either by recrystallization from petroleum ether or by vacuum distillation, followed by recrystallization.

1, 1-Diaryl-1, 2, 2-trichloro-2-fluoroethane (**III**). A mixture of 0.07 mol of II, 12 g (0.1 mol) of thionyl chloride, and 8 g (0.1 mol) of pyridine was refluxed After being cooled, the reaction mixture for 2hr. was poured onto ice, and the product was extracted with ether. The ether was removed by distillation, and the residue was purified by vacuum distillation and/or recrystallization from petroleum ether.

1, 1 - Diaryl - 2 - chloro - 2-fluoroethylene (IV). A mixture of 0.016 mol of III, 1.5 g (0.023 g-atom) of zinc dust, and 20 ml of ethanol was refluxed for 3hr in the presence of a catalytic amount (50-100 mg) of zinc chloride, and then filtered. After the removal of the ethanol from the filtrate by distillation, the residue was distilled in vacuum and/or recrystallized from petroleum ether.

Aryl Dichlorofluoromethyl Ketone (VI). To a Grignard solution prepared from 0.3 mol of an aryl bromide, 7.5 g (0.3 g-atom) of magnesium, and 300 mlof ether, 0.25 mol of V was added gradually with stirring at -5 to 0°C. The product was isolated by the hydrolysis of the reaction mixture, followed by the vacuum distillation of the organic layer.

1-Aryl-2, 2-dichloro-2-fluoroethanol (VII). To a suspension of 2.5 g (0.065 mol) of lithium aluminum hydride in 120 ml of ether, a solution of 0.16 mol of VI in 80 ml of ether was added dropwise with stirring below 0°C. After the excess hydride had been decomposed with water and hydrochloric acid, the ethereal layer was distilled in vacuum.

1-Aryl-1, 2, 2-trichloro-2-fluoroethane (VIII). A mixture of 0.077 mol of VII, 12 g (0.1 mol) of thionyl chloride, and 8 g (0.1 mol) of pyridine was refluxed for 2hr, and then worked up as has been described above for III.

1-Aryl-2-chloro-2-fluoroethylene (IX). A mixture of 0.01 mol of VIII, 1.5 g (0.023 g-atom) of zinc dust, a catalytic amount of zinc chloride, and 20 ml of ethanol was refluxed for 3hr, and then filtered. The vacuum distillation of the filtrate gave a mixture of two isomers, IXa and IXb, the ratio of which was determined by v.p.c. (Apiezon-L 5%, 3m) on the assumption that the molar responses of IXa and IXb were equal. Generally IXa had a shorter retention time than IXb.

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